Enrichment processes of arsenic in oxidic sedimentary rocks – from geochemical and genetic characterization to potential mobility

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Abstract

Sedimentary marine iron ores of Jurassic age and Tertiary marine sandy sediments containing iron hydroxides concretions have been sampled from boreholes and outcrops in two study areas in Germany to examine iron and arsenic accumulation processes. Samples were analyzed for bulk rock geochemistry (INAA/ICP-OES), quantitative mineralogy (XRD with Rietveld analysis), element distribution (electron microprobe) and arsenic fractionation (sequential extraction). Bulk Jurassic ores contain an average arsenic content of 123 µg g^{-1} hosted in mainly goethite ooids which slowly formed in times of condensed sedimentation. Enrichment occurred syndepositionally and is therefore characterized as primary. Iron concretions in Tertiary sediments mainly consist of goethite and yield arsenic up to 1860 µg g^{-1}. The accumulation process is secondary as it took place in the course of oxidation of the originally reduced marine sediments under terrestrial conditions, leading to element redistribution and local enrichment in the near-surface part. The scale of enrichment was assessed

calculating Enrichment Factors, indicating that arsenic accumulation was favoured over other potential contaminants. In spite of higher bulk arsenic contents in the oxidic rocks, the mainly pyrite-hosted As pool within the reduced deeper part of the Tertiary sediments is shown to have a higher potential for remobilization and creation of elevated arsenic concentrations in groundwater.

Keywords

arsenic, accumulation process, iron mineral, enrichment factor, redox conditions, mobilization

1 Introduction

1.1 Background and objectives

During the past two decades, the intensity of arsenic (As) research has increased substantially. Reasons for that are the recognition of As toxicity and its initially underestimated impact on human health on a global scale, focussing on large problem areas, especially in Southeast Asia (e.g. Ravenscroft et al. 2005, Zahid et al. 2009). Consequently, drinking water threshold values were broadly lowered in the 1990ies, mostly down to 10 µg L^{-1}. This confronted water suppliers with the problem of an increased need to process raw water in order to match drinking water requirements. In recent years, it was also found that in the large majority of cases, naturally occurring As is responsible for elevated groundwater concentrations. Thereby, mobilization from As-enriched minerals is the dominating process (e.g. Lowers et al. 2007, Armienta et al. 2001). Showing characteristics of both chalcophile and siderophile behaviour, arsenic tends to be preferably hosted by sulphide minerals like pyrite or (hydr)oxidic Fe phases like goethite, both of which can contain As up to several wt.% (Smedley and Kinniburgh 2002). In spite of its low average abundance in the upper earth´s crust (1.5-2 µg g^{-1}; Matschullat 1999), arsenic can accumulate in rocks to concentrations several orders of magnitude higher than this value. The fate of As in the environment is controlled by the prevailing physico-chemical conditions and the presence of other ions. Redox potential, pH and ionic competition are crucial parameters governing As behaviour (adsorption, desorption, transport, redox

53 transformation). Reducing conditions can lead to As mobilization from oxides while oxidizing
54 conditions may mobilize As bound to sulphides. High groundwater pH constrains As adsorption to
55 mineral surfaces and may therefore be responsible for elevated concentrations in solution. Ions
56 competing with As species for surface binding sites, especially phosphate, can lead to the same result
57 (Stollenwerk 2002, Smedley and Kinniburgh 2002).

58 The basis to understand geogenic As cycling and the impact of water-rock-interaction leading to
59 groundwater contamination is the comprehension of the mechanisms that led to those accumulations,
60 i.e. arsenic enrichment processes. These often took place millions of years ago, but still have a major
61 influence on the recent occurrence and thus, hydrogeochemical behaviour, of As and other potential
62 groundwater contaminants.

63 While As accumulation in Southeast Asia is subject to extensive research and ongoing lively
64 discussions (e.g. Acharyya et al. 2000, Stanger 2005), little is known about the origin and development
65 of geogenic As accumulations in Germany which have been studied sporadically and on a rather local
66 to regional scale (e.g. Bayer 1997, Heinrichs and Udluft 1999, Rüde and Königskötter 2009, Banning
67 et al. 2009), although elevated As concentrations have been detected in many parts of the country, an
68 overview is given by Heinrichs and Udluft (1996).

69 In this study, we analyzed and compared As-bearing sedimentary rocks in two study areas in Germany
70 and deduced the relevant accumulation processes, taking hydrogeochemical, mineralogical and
71 paleogeographical information into account, evaluating the scale of enrichment and estimating the
72 consequences for potential As remobilization and output into groundwater.

73

74 1.2 Study areas

75 Two investigation areas in Germany were selected for rock sampling in the Upper Rhine Graben and
76 in the Lower Rhine Embayment, respectively (Fig. 1).

77

78 Figure 1 Location of study areas in Germany (right side) and geological overview maps with sampling locations
79 in the Lower Rhine Embayment (LRE; upper left side) and the Upper Rhine Graben (URG; lower left
80 side).

81

82 1.2.1 Upper Rhine Graben (URG)

83 The URG is an approximately NE-SW-striking rift structure in the border area between Germany and
84 France. It is situated in between the crystalline basement areas of the Black Forest (Germany) and the
85 Vosges mountains (France) and mainly filled with sediments of Tertiary age (Fig. 1). Along the
86 fringes, within the contact zone between crystalline basement and basin filling, shallow marine
87 Jurassic rocks crop out hosting several horizons of sedimentary-marine ooidic Fe ores which can be
88 found for ~150 km along the basin margin (Sauer and Simon 1975). During the break-in of the URG,
89 starting in the early Tertiary and being active to date, steep marginal faults developed and the Jurassic
90 sediments disrupted and today represent the base rock of the Cenozoic graben filling. In the better
91 accessible marginal part, the sedimentary Fe ores, deposited in the middle Jurassic (Aalenian), were
92 mined until the 1960ies. One former location of surface Fe ore mining, the Kahlenberg (~30 km north
93 of Freiburg, mined until 1969 and today serving as a waste disposal site, Fig. 1), offers a nearly
94 complete succession of sedimentary rocks from the middle Jurassic (Fig. 2) and was therefore chosen
95 for sampling.

96

97 1.2.2 Lower Rhine Embayment (LRE)

98 The LRE is part of the northwest European Tertiary basin which ranges from the British Isles to
99 Poland. Similar to, and in continuance of, the URG, it represents a rift structure starting its break-in in
100 middle Tertiary. It is mainly filled with Tertiary marine sediments deriving from the uplift and
101 subsequent erosion of the surrounding Rhenish Massif. The basin strikes NNW-SSE (Fig. 1). The
102 graben filling comprises a relatively complete succession of Oligocene, Miocene and Pliocene
103 sediments which have variable thicknesses due to extensional fault tectonics and the crust breaking
104 apart into several blocks. The Grafenberg-layers of the Upper Oligocene (Chattian) are very
105 widespread within the LRE. They represent marine fine sands with a significant thickness of several
106 hundred meters due to a high sea level and a quite rapid basin floor subsidence during the Chattian
107 (GLA NRW 1988, Hiss et al. 2005). The primary calcareous and glauconitic Grafenberg-layers

underwent deep terrestrial weathering in the Late Tertiary. This way, they were altered to a depth of several decametres in terms of losing their calcitic cement and having their Fe(II) mineral phases oxidized. Iron was mobilized and accumulated as Fe(III) hydroxides in the oxidized upper part. The redox boundary is not observable in outcrops nowadays, but was described from former quarries and boreholes by Quaas (1917). He documented it mainly between 20 and 30 m, in one outcrop in only 6 m depth below ground surface. The geological development and present situation is similar to the one described for the southwestern Münsterland Cretaceous Basin (Banning et al. 2009). The reduced lower part of the Grafenberg-layers was sampled from boreholes near Willich and Hamminkeln, the oxidized upper part from two outcrops of these sediments near Süchteln (Fig. 1).

2 Material and methods

2.1 Material

From the Jurassic sedimentary profile at the Kahlenberg, 32 rock samples were obtained, covering a sediment thickness of ~34 m and crossing the stratigraphical boundary between Aalenian (Dogger β) and Bajocian (Dogger γ) (Fig. 2). Out of these samples, 11 are from the main Fe ore body (*murchinsonae* ore horizon) and 7 from two thinner Fe ore layers. In the following, the sampled profile is shortly described. The stratigraphical terms are mainly from Bayer (1970), derived from biozone classification by ammonites.

The profile starts at the bottom with clays (*opalinus* clay) and calcareous sandstones (lowest Aalenian), both of which were not accessible for sampling. Subsequently, the main ore body ("Haupterzlager" – HEL) follows with a thickness of ~11 m. The ore consists of Fe phase ooids in mainly calcitic cement. It is very fossiliferous, especially containing echinoderm remains. Sedimentological studies showed that Fe ooid formation occurred in a shallow marine environment with long-term relatively stable flow velocities in a facies transition zone between rather carbonate-dominated and more sandy sediments. The latter can be found some kilometres north of the Kahlenberg outcrop, arguing for higher flow velocities, lower water depths and proximity to the coastline (Aldinger 1957; Urban 1966). Clastic and Fe input into the system are estimated to derive

from terrestrial weathering of the Rhenisch-Ardennic Shield in the north (Sauer and Simon 1975). The *staufensis* zone, containing the *murchinsonae* ore, is followed by the *concava* zone composed of marlstones ("Gryphitenmergel" – GM; ~2 m), sandstones ("Wedelsandstein" – WS; ~6.5 m) and the lower ore layer (LOL; ~0.7 m). The latter comprises Fe ooids in carbonatic matrix again, and thus indicates the return of favourable conditions for Fe accumulation. An omission surface on top of this layer contains the Aalenian-Bajocian stratigraphic boundary. Above that, clayey marlstone (~1.5 m; not sampled), the upper ore layer (UOL; ~0.7 m; macroscopically similar to the lower one), a mudstone ("Rimsinger Ton" – RT; ~6 m) and limestone layer ("Hangende Kalke" – HK; ~2.5 m) belong to the *hyperlioceras* and the *sowerby* zone. The Jurassic rocks in the area are covered by Pleistocene loess with a thickness of up to 10 m.

From the range of the Grafenberg-layers in the LRE, a total number of 36 sediment samples were taken, 16 of which stem from the reduced lower part and were sampled from cores of up to 182 m deep boreholes (in addition, one sample of the Quaternary cover sediment – coarse sand – was taken for comparison). All borehole samples were sealed in gastight bags and stored at 4° C. The remaining 19 samples were obtained from two outcrops of the oxidized upper part of the Grafenberg-layers.

The reduced lower facies of the Grafenberg-layers comprises a quite homogenous marine fine sand of greyish to greenish colours with a total thickness of up to ~300 m in the study area (Nickel 2003). They are little consolidated and contain calcite, glauconite and abundant mollusc shells. Sediment habit hardly changes on a length of ~140 m in the sampled core (with an important exception in the uppermost section of the strata which is discussed later on), documenting relatively stable shallow marine depositional conditions during the Chattian. Clastic input into the basin derived from the weathering of Variscan mainlands to the east of the LRE.

Resulting from the paleo-redox process mentioned in the previous chapter, the oxidized upper facies of the Grafenberg-layers is composed of yellowish to orange fine sands. They are unconsolidated due to the loss of their carbonatic cement. Iron mobilized from reduced phases during the late Tertiary weathering precipitated in the upper part, forming Fe(III) hydroxide coatings around quartz grains. In outcrops, Fe(III)-concretions are observable which are orange to dark red in colour and significantly

more consolidated than the ambient sands. Special attention was paid to these concretions during sampling.

2.2 Methods

Bulk rock geochemistry (55 elements) was assessed for all (68) samples using either Instrumental Neutron Activation Analysis (INAA; thermal neutron flux: $7*10^{12}$ n cm^{-2} s^{-1}; Ge detector: resolution better than 1.7 keV for the 1332 keV, ^{60}Co photopeak) or total digestion ($HClO_4$-HNO_3-HCl-HF at 240°C) followed by analysis with ICP-OES (Varian 735ES).

Seventeen selected samples (five Jurassic ore samples, five samples from the reduced part of the Grafenberg-layers, seven from the respective oxidized part) were ground to powder grain size in a corundum mill and their mineralogical composition was determined using a Bruker AXS D8 Advance X-ray diffractometer (XRD; operational adjustments: 40 kV, 40 mA; 2θ=2-92°). Quantitative mineral phase analysis was accomplished applying Rietveld analysis with the software BGMN, version 4.2.3.

Thin sections were produced from five Fe ore samples (three from the main ore body – lower, middle and upper part – and one from the lower and upper ore layer, respectively). These were studied and photographed using a reflected-light microscope (Leica MZ75). Additionally, two thin sections (upper and lower part of the main ore body) were analyzed for element distribution with an electron microprobe (EMP, JEOL JXA-8900R, equipped with energy-dispersive and wavelength-dispersive spectrometers, and operated at 15 kV and 23 nA with a beam diameter of 1.6 µm). Qualitative chemical mapping was performed for Si, Ca, Fe, Mn and As to characterize element distribution between the main rock components (ooids, matrix, clastic grains). Moreover, a traverse of quantitative single spot measurements was produced to assess chemical distribution in the single ooid grain scale, i.e. in the nucleus and the cortex.

Arsenic fractionation and mobilization potential were examined applying a sequential extraction procedure (SEP), designed for As by Wenzel et al. (2001). It was modified accounting for sample composition, i.e. two additional steps, targeting for As bound on Mn (hydr)oxides and sulphides, respectively, were implemented for samples with significant Mn or S (as pyrite) content, see chapter

189 3.1. Altogether, the applied procedure consisted of six steps (Tab. 1). A total of 20 samples were
190 involved in the sequence (eight from the Jurassic sedimentary profile, four from the reduced Tertiary
191 sediments, eight from their oxidized facies). The pulverized (agate mortar) solid sample (2 g) was
192 placed in centrifugation tubes. Successively, 50 mL of each extraction reagent was added and the
193 respective extraction procedure for each step was carried out. The tube was then centrifuged at 3000
194 rpm for 15 minutes and subsequently, the supernatant solution was filtered through 0.45 µm cellulose
195 acetate filters. The remaining solid material was then used for the next extraction step. Analysis of
196 dissolved As was performed using AAS (Perkin Elmer AAnalyst 800, THGA furnace).

197

198 Table 1: Sequential Extraction Procedure.

199

200 3 Results

201 Obtained results are presented in this chapter, distinguishing between Jurassic and Tertiary sediments
202 in the subsections.

203 3.1 Bulk rock geochemistry and mineralogy

204 3.1.1 Jurassic sediments

205 Contents of elements relevant for this study in the sampled Jurassic rocks as determined from
206 INAA/TD-ICP analysis as well as MUNSELL sample colour characterization are shown in Table 2.
207 Figure 2 illustrates the development of Fe and As as well as Fe phase fractionation in the sediment
208 profile at the Kahlenberg.

209

210 Table 2: Whole rock geochemical results of selected elements from the Jurassic samples (DL: detection limit;
211 HK: Hangende Kalke, limestone; RT: Rimsinger Ton, mudstone; UOL: upper ore layer, LOL: lower ore
212 layer; WS: Wedelsandstein, sandstone; GM: Gryhitenmergel, marlstone; HEL: Haupterzlager, main Fe
213 ore body). Samples marked with grey background were analyzed with XRD, see also Table 3.

214

215 Iron overall average content for the ore layers is 17.8 ± 7.0 wt.% while the non-ore sediments show an
216 average of 2.2 ± 1.1 wt.%. The three different ore horizons contain 14.1 ± 3.0 wt.% (UOL), 11.6 ± 1.2

wt.% (LOL) and 21.3 ± 6.9 wt.% (HEL), respectively. Arsenic in all ore samples is present at 123 ± 48.5 µg g^{-1} (UOL: 131 ± 21 µg g^{-1}; LOL: 97 ± 11 µg g^{-1}; HEL: 133 ± 59 µg g^{-1}), in the remaining sediments at 18.0 ± 7.8 µg g^{-1}. Iron and As development with depths exhibit a close positive correlation (Fig. 2). Trace metals contents in single samples and average values for the different stratigraphical layers are shown in Table 2.

Figure 2: Lithological profile, Fe and As contents development and Fe phase fractionation of the sampled Jurassic sediments, former quarry Kahlenberg.

The mineralogical composition of the ooidic Fe ores, calculated from X-ray diffractograms using Rietveld analysis is summarized in Table 3. Iron phase fractionation is additionally indicated in Figure 2. Goethite (α-FeOOH) is the most important Fe host mineral in the ore layers, accounting for 67 ± 9 % of the present Fe phases, whereby the proportion is slightly higher in the ore layers, compared to the main ore body. Other Fe phases, hematite (α-Fe_2O_3; 23.8 ± 16 %) and the Fe silicate mineral chamosite ($(Fe^{2+},Mg,Fe^{3+})_5Al(Si_3Al)O_{10}(OH,O)_8$; 8.8 ± 10 %), show much higher variabilities. Hematite is more abundant in the main ore body, while chamosite reaches significant amounts in the ore layers only (Fig. 2). Besides Fe host minerals, bulk ore samples contain calcite ($CaCO_3$) as the main matrix mineral, detrital quartz (SiO_2) and minor amounts of muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$) and microcline ($KAlSi_3O_8$). Dolomite ($CaMg(CO_3)_2$) is partly detectable, pyrite (FeS_2) is present in trace amounts in the two thinner ore layers only.

Table 3: Mineralogical composition of Jurassic Fe ore samples, see Tab. 2 for stratigraphical allocation (n.d. – not detectable).

In all Fe ore thin sections, oval to nearly round ooid grains of brownish to reddish colour in a mainly greyish calcitic matrix were observed. In some parts, the latter is of yellowish-orange colour, indicating matrix areas with elevated Fe. Sub-rounded detrital quartz grains and bioclasts are further components. Among the fossils found in the samples, echinoderms, especially crinoids, are most abundant. Additionally, gastropoda, bivalvia, bryozoa, foraminifera and one calcite-filled belemnite

246 rostrum were found. Some Fe grains exhibit characteristics of broken and regenerated ooids. It can be
247 assumed that during ooid formation, the milieu underwent multiple synsedimentary reworking and
248 redeposition as also indicated by ooids forming the nucleus of the next ooid generation (Flügel 2004).
249 Bioclasts serve as further nucleus material. Despite their abundance in the ores, silicate (mainly
250 quartz) grains were not found as nuclei, which is in agreement with Jurassic ooidic Fe ores from the
251 Swiss Jura mountains (Burkhalter 1995). Thin section analyses indicate that the samples are rather
252 matrix-supported (matrix/component ratios range from ~80/20 to 50/50, with HEL ores showing a
253 higher component proportion). The carbonatic matrix is micritic in UOL and LOL, whereas it is rather
254 sparitic in HEL, arguing for a higher degree of cementation. This is supported by a lower amount of
255 bioclasts and a higher proportion of hematite, possibly formed through dehydration of primary
256 goethite or its precursor phases (Maynard 1983, Schwertmann et al. 1999), compared to the thinner ore
257 layers.

258

259 3.1.2 Tertiary sediments

260 Table 4 shows the geochemical composition of sediments from the Grafenberg-layers. A concentration
261 profile indicates geochemical development of some elements and Fe phase fractionation dependent
262 upon depth in the borehole (Fig. 3).

263

264 Table 4: Whole rock geochemical results of selected elements from the Tertiary sediments (DL: detection limit;
265 Ox_G: oxidized Grafenberg-layers; QC_G: Quarternary cover sediment; Red_G: reduced Grafenberg-
266 layers; Red_H: Reduced Grafenberg-layers from the borehole in Hamminkeln). Samples marked with
267 grey background were analyzed with XRD, see also Table 5.

268

269 The reduced lower part of the Grafenberg-layers contains relatively homogenous Fe and As of 1.84 ±
270 0.57 wt.% and 11.6 ± 3.6 µg g^{-1}, respectively. Sulphur content is 0.22 ± 0.09 wt.% on average, it
271 correlates well with As for a large part of the profile (Fig. 3).

272

273 Figure 3: Stratigraphical profile, Fe, As and S contents development and Fe phase fractionation of the
274 Grafenberg-layers sampled from a borehole near Willich.

275

Bulk sediment mineralogical results can be found in Table 5. Moreover, Figure 3 contains Fe phase fractionation in borehole samples. XRD analysis identified several reduced Fe minerals, wherein glauconite ($(K,Na)(Fe,Al,Mg)_2[(OH)_2|(Si,Al)_4O_{10}]$) is dominant (60 % of all Fe phases on average), followed by pyrite (FeS_2) and siderite ($FeCO_3$). Greenish glauconite and framboidal pyrite grains were observable in the sediments under the microscope. One layer at the bottom of the borehole contains a high glauconite proportion of 11.1 % of the bulk sample. Goethite (FeOOH) was identified in the uppermost Tertiary sample (GW_0201) only, coexisting with siderite, glauconite and pyrite and thus indicating a zone of redox transition. The calcite content here (0.09 %) is depleted, compared to the deeper sediments (1.82 ± 0.79 %); on the other hand, Fe and As are enriched by factor 3 and 2, respectively. The discordantly following Quarternary cover sediments yield significantly lower contents of Fe and As (Fig. 3). Besides quartz as the dominant mineral phase, calcite and the mentioned Fe phases (Tab. 5), the samples contain minor amounts of muscovite, clay minerals and feldspar.

Table 5: Mineralogical composition of Grafenberg-layers samples, see Tab. 4 for facies allocation (n.d. – not detectable).

In contrary to the deep sediments, the upper oxidized facies of the Grafenberg-layers shows a very heterogenous distribution of Fe, As and other trace elements, so mean values are not given in Table 4. Iron content averages 3.93 ± 2.2 wt.% in the unconsolidated sands, but can be as high as 23.4 wt.% in concretions. All samples contain goethite whose proportion ranges from 1.04 to 34.51 %. Lepidocrocite (γ-FeOOH) as a second Fe hydroxide was identified in two samples. XRD analysis of one sample in the grain fraction <0.63 µm (GG_0102f; obtained through wet sieving) indicated that Fe hydroxides are preferably occurring in the fine-grained sediment proportion. Calcite is not detectable in any sample (Tab. 5).

Arsenic contents average 20.3 ± 11.8 µg g^{-1} in sands, but yield a peak value of 1860 µg g^{-1} As in one Fe concretion, thus underlining the pronounced heterogeneity of element distribution in the oxidized facies, even at very close range (Fig. 4).

Figure 4: Example of heterogenous Fe and As distribution in the oxidized part of the Grafenberg-layers. The inset (upper left corner) shows Fe concretions found in the darker (orange) layer on the left side.

In the example shown in figure 4, Fe and As levels increase erratically from hardly coloured (right side) via bright orange sands (left side) to the very hard, dark reddish Fe concretions (inset) found within the latter. Approximate relational factors in these three sediment zones for Fe are 1-2-17, for As 1-5-207. The different scales of enrichment, also for other trace elements, are discussed in chapter 4.2.

3.2 EMP results in Fe ores

Results of the chemical mapping of an ooid grain from the upper part of the main ore body conducted with energy-dispersive microprobe analysis are shown in Figure 5a. The general detection limit for this method is approximately 0.5 wt.%. The mapping area was chosen to contain all important sediment components (Fe ooids, carbonate matrix, clastic grains). For As, the resulting map was homogenous, thus not showing any differences in As distribution. This suggests that As is present in contents <0.5 wt.% in all rock compounds. To assess As contents in the ooid grains, a traverse of quantitative wavelength-dispersive single spot measurements was carried out (Fig. 5b). Detection limit for As in this procedure was calculated to be 117 $\mu g\ g^{-1}$.

Figure 5: a: elemental mapping of an Fe ooid in calcitic matrix (qualitative), b: traverse (indicated in backscattered light image) of single spot chemical measurements through cortex and nucleus of an Fe ooid.

Element distribution maps (Fig. 5a) show a well-definded oval Fe ooid (Fe map) from the HEL, together with matrix material and margins of two silicate grains (Si map). Calcium is present in the matrix only. Besides the detrital grains, Si occurs in smaller amounts in some areas within the ooid. The distribution of Mn indicates its preferential presence in the matrix rather than in the ooid. Iron distribution within the ooid is not even, differences correspond to different layers of the cortex, the ooid rim seems to be particularly enriched. In the case of Figure 5a, the nucleus is Fe-rich (although it

seems to contain less Fe than the average cortex), thus probably representing an ooid fragment of a previous generation. A profile of point measurements, shown for another Fe ooid in Figure 5b (backscattered light), supports these findings. Iron is enriched in the "lighter" parts (areas of higher electron density) of the cortex and in the nucleus, exceeding 50 wt.%, while the "darker" layers contain around 40 wt.% Fe. On the contrary, Al and Si are more abundant in the darker parts. Unlike in the "macroscopic" outcrop scale (Fig. 2), arsenic contents do not necessarily follow Fe in the grain scale. While, independent from Fe, arsenic content is around 1000 µg g^{-1} in the cortex layers, it drops to below 500 µg g^{-1} in the nucleus.

3.3 SEP results

Sequential extraction procedures base on using increasingly stronger solvents, each targeting a specific host mineral fraction (Tab. 1) which allows us to subdivide the bulk trace element (in this case As) content of a sample into proportions of different extractabilities. This enables an estimation of the potential mobility of As and is thus more valuable for ecological considerations than the bulk content.

3.3.1 Jurassic sediments

Results of As fractionation determined by SEP are shown in Figure 6a. An average proportion of 3.64 ± 1.9 % As_{tot} is surface-bound (i.e. $NH_4H_2PO_4$-soluble and thus quite readily available through pH changes or P addition, Wenzel et al. 2001) in Fe ore layers, corresponding to more variable absolute amounts of 1.9-10.3 µg g^{-1}. Mudstone (RT) and sandstone (WS) from the Jurassic sediment profile both show comparable relative proportions of 3.7 %, but absolute As amounts of only 0.8-1.5 µg g^{-1} soluble in step 1. Arsenic bound to Mn (hydr)oxides, targeted with NH_2OH-HCl (step 2), is of minor importance (0.69 ± 0.4 % in ore layers). NH_4-oxalate-soluble As (step 3) is most important in RT mudstone (27 %), fresh Fe hydroxide striation was observable in the sampled sediments. The As proportion dissolved in this step is higher in UOL and LOL (~13 %) than in HEL (~7 %, decreasing towards the lower part). Arsenic fractions of lower extractability (step 4 and step 6) are dominant in all ore layers. Within HEL, residual As increases with depth. Step 5-soluble As is negligible except for

RT (8.5 %). Assuming a change in redox conditions from presently oxidizing to rather reducing conditions, the potentially short- to medium-term mobilizable As amount corresponds to steps 1-3 soluble As (Banning et al. 2009). This proportion is higher for the thinner ore layers (~18 %) than for HEL (~11 %), nevertheless, corresponding maximum absolute values are comparable (Fig. 6a).

Figure 6: Sequential extraction results of samples from the Jurassic profile (a) (RT: Rimsinger Ton, mudstone; UOL: upper ore layer, LOL: lower ore layer; WS: Wedelsandstein, sandstone; HEL: Haupterzlager, main Fe ore body) and selected Tertiary sediment samples (b), ordered by redox facies.

3.3.2 Tertiary sediments

Sequential extraction results for samples from the range of the Grafenberg-layers are illustrated in Figure 6b. The reduced lower part of the Grafenberg-layers comprises a relatively homogenous As fractionation. Arsenic soluble in step 1 is 7.30 ± 0.4 %, 31.89 ± 2.1 % in step 3, 28.76 ± 5.2 % in step 4 and 27.47 ± 5.6 % in step 5. In the redox transition zone, H_2O_2-soluble As decreases to 16 %. Potential mobilizability is similar in all samples (38.57 ± 2.3 % As_{tot}), but higher absolute amounts are found in the transition zone (Fig. 6b).

Arsenic extractability in the oxidized facies is more heterogenous. Fractions of steps 4 and 6 are dominant in all samples, but proportions of higher extractability (steps 1-3) vary heavily in unconsolidated sands (5.9-33.1 %) as well as in harder concretions (3.4-39.1 %). Corresponding potentially mobile As varies between 1.3 and 62.6 µg g^{-1} with a peak value for Fe concretion GG_0103 (Fig. 6b).

4 Discussion

The Discussion chapter distinguishes between Jurassic and Tertiary sediments in the three subsections 4.1-4.3, before a comparison is drawn in the Conclusions chapter 5.

4.1 Geochemical characterization and timing of As accumulation

4.1.1 Jurassic sediments

387 The studied Fe ores from the former quarry Kahlenberg represent a significant As sink with a
388 maximum content of 223 µg g^{-1} at 32.2 wt.% Fe in HEL. The overall average of the ore samples (123
389 µg g^{-1}) is elevated by ~factor 7, compared to the non-ore sediments of the profile. Lithologically and
390 facially similar Jurassic ooidic Fe ores from Luxemburg and France (so called Minette Fe ores) are
391 known to be potential As hosts: Siehl and Thein (1978) detected maximum As contents of 435 µg g^{-1}
392 at 50 wt.% Fe in one profile (with As and Fe correlating well), thus showing conditions comparable to
393 the ooid ores studied in this work. The scale of As (and other elements) enrichment is discussed in
394 more detail in chapter 4.2.1.

395 Statistical analysis of ore samples from the main ore body (HEL) was conducted using the software
396 SPSS Statistics 17.0. A matrix of Pearson element correlations is presented in Figure 7a.

397

398 Figure 7: Pearson element correlation matrices for samples from the HEL (a) and the oxidized facies of the
399 Grafenberg-layers (b).
400

401 Arsenic occurrence and behaviour is controlled by Fe oxides and hydroxides, as suggested by
402 mineralogical and sequential extraction results, as well as element correlation analysis (Fig. 7a).
403 Goethite was found to be the most important Fe host phase, which is in agreement with previous
404 studies about these ores (Aldinger 1957, Sauer and Simon 1975). This is also valid for similar ooidic
405 Fe accumulations of Aalenian/Bajocian age from Switzerland described by Burkhalter (1995). In that
406 study, also chamositic ooids were found, forming a complete transition series with goethite ooids.
407 Varying degrees of the chamosite compound in predominantly goethite ooids might explain the
408 occurrence of elevated Si in some areas of the ooid studied with EMP (Fig. 5a), Al and Si enrichment
409 in the "darker" layers of the cortex (Fig. 5b) as well as a positive Fe-Al correlation (Fig. 7a). Another
410 similarity is a comparably high P content in the Fe ore layers (0.3 wt.% on average in this study),
411 attributable to apatite admixtures in the ooids on a submicroscopic scale (Burkhalter 1995). This is
412 supported by a very significant positive correlation between Fe and P (Fig. 7a), indicating that P is
413 hosted by Fe ooids. However, apatite was not detectable in XRD, making it more likely that P is
414 present on the Fe (hydr)oxide surfaces as it was described for Jurassic Fe ooids in Bavaria (Halbach

1968). Most probably, it was adsorbed as PO_4^{3-} from sea water during the precipitation of positively charged $Fe(OH)_3$ particles.

In contrast to P-Fe, Ca correlation with Fe is significantly negative. Calcium is present in the calcitic matrix only, while Fe is broadly limited to ooid grains (although microscopy of thin sections revealed some areas of visible Fe contribution to the matrix material). The only studied element with a positive relationship towards Ca, and therefore most probably hosted predominantly in the matrix, is Mn. It correlates significantly negative with all other metals, As and P and thus indicates its absence in the Fe ooids. These findings are supported by elemental mapping in EMP (Fig. 5a) and the lack of As bound to Mn (hydr)oxides as suggested by SEP (Fig. 6a). Consequently, although Mn mineral phases can yield a major influence on As behaviour (Smedley and Kinniburgh 2002), they do not do so in the case of the studied ores. An explanation for this phenomenon might be the formation of weakly reducing microenvironments caused by bacterial decomposition of organic matter in the sediments. This may lead to Mn release from the solid phase to solution and subsequent uptake by the calcite matrix, while Fe^{2+} remained in the form of chamosite (the presence of chamosite is interpreted as a proxy for mildly reducing conditions during diagenesis, Berner 1981). A mechanism like that is proposed for Tertiary Fe ooids in Egypt (Salama et al. 2008). During the latest period of Fe ooid formation in the studied profile (i.e., in the UOL), stronger reducing conditions seem to have been prevailing, indicated by trace amounts of pyrite and a high proportion of chamosite among Fe phases (Fig. 2).

In contrary to Mn, Pb, Zn, Co, Cd, Cr and Ni correlate positively with Fe and As, and with each other, and negatively with Ca and Mn, clearly indicating that these heavy metals are hosted by Fe ooids, and hardly appear in the matrix. The correlation of Fe and As is weaker at the grain scale as deviated by single ooid measurements (Fig. 5b). This suggests that conditions for As accumulation varied before (ooid nuclei), during (ooid cortices) and after (matrix) Fe ooid formation.

Element and mineral distribution in the studied sediments argue for a primary, i.e. syndepositional accumulation of As in Fe ooids from the middle Jurassic. Shallow marine origin of the ores under tropical climatic conditions is evident from the fossil record (chapter 3.1.1; Urban 1966). Iron (and As) accumulation in the present form occurred in times of non-deposition (concerning clastic input, i.e. in condensed horizons) in at least temporarily agitated water, which are prerequisites for Fe ooid

443 formation (Burkhalter 1995). Under these conditions, Fe together with As and trace metals, was
444 transported in solution or colloidal form from the weathering mainland towards shallow marine
445 environments. There, it was able to accumulate, before conditions changed once more and the calcitic
446 matrix settled. During the slow process of Fe ooid formation, reactive surfaces were available for a
447 long time for AsO_4^{3-} adsorption on hydroxides as described above for the geochemically very similar
448 PO_4^{3-}. Additionally, these surfaces were renewed through rhythmic formation of ooid cortices and
449 periodical reworking of the sediments. This way, syndepositional As enrichment potential in Fe ooids
450 is obvious. After the main accumulation (HEL), a sedimentary milieu favouring Fe and As enrichment
451 returned twice as documented by LOL and UOL.

452

453 4.1.2 Tertiary sediment

454 The oxidized upper part of the Grafenberg-layers, compared to the reduced lower part, is enriched in
455 As by ~factor 2, considering average values. However, due to the extremely heterogenous element
456 distribution, the scale of enrichment has to be analysed in more detail (chapter 4.2.2). Like for the
457 Jurassic samples described in chapter 4.1.1, statistical analysis for the oxidized near-surface facies of
458 the Grafenberg-layers was conducted using SPSS software. The Pearson element correlation matrix is
459 shown in figure 7b. Due to its partly extremely high concentrations, especially for Fe and As,
460 concretion GG_0103 was not included in the calculations. Like in the Fe ooids, a striking positive
461 correlation (R^2=0.93) between Fe and P is observable – again, P is bound to Fe hydroxides (goethite
462 and, less abundant, lepidocrocite), ubiquitarily available in the oxidized sediments. Iron correlations
463 with metals are variable. While Cd (R^2=0.96), Zn (R^2=0.80) and, less distinct, Cr (R^2=0.60) show a
464 clear positive relation towards Fe, regression is much weaker for Ce (R^2=0.39), Mn (R^2=0.37), Co
465 (R^2=0.37), Pb (R^2=0.31), As (R^2=0.30) and Ni (R^2=0.21) and is not detectable for Cu and Al. From the
466 second group, Mn, Co, Ni and Ce provide positive interrelations (R^2=0.63-0.97) arguing for a common
467 occurrence, while Cu, Al and As do not yield any significant correlation with the other metals. These
468 results underline the extreme heterogenous element distribution. Nevertheless, the lack of As-Al
469 correlation and SEP results indicate that no clay minerals or other silicates but rather Fe hydroxides act
470 as As sinks, albeit with large variations in adsorbed As amounts. The by far highest As content has

been measured in the most Fe-rich sample (Fig. 4). In a similar geological environment showing pronounced post paleo-redox elemental redistribution, Banning et al. (2009) found As being accumulated in Fe hydroxide concretions without yielding any correlation with bulk Fe.

The source of near-surface Fe (and As) is believed to be the reduced Fe phases from the deeper sediments, i.e. the primary depositional facies, nowadays only accessible in boreholes. Several "candidate" minerals were identified by XRD: glauconite, pyrite and siderite, additionally goethite was detected in the uppermost Tertiary sample GW_0201, indicating a redox transition zone (chapter 3.1.2). The potential role of the reduced Fe phases for As behaviour in the Tertiary sediments will be discussed in the course of a short literature overview in the following.

Glauconite has the highest proportion in Fe phases in the fully reduced sediments, whereas siderite seems to be more abundant in the oxidation cap (Fig. 3). Greensands containing significant amounts of glauconite are known to have a potential for As accumulation. Dooley (1998) found As contents in New Jersey greensand one order of magnitude higher than in average soils of the area. Barringer et al. (2009) consider these glauconites as one source of elevated As concentrations in groundwater. In a creek near Brussels, Belgium, Cappuyns et al. (2002) detected As accumulations in soil Fe hydroxides and attributed them to mobilization from As-rich glauconites in the subsurface. Patyk-Kara et al. (2008) found "abnormally high As" contents in glauconite samples from central Russia. Conducting SEM analysis of single grains, they measured up to 72 wt.% (!) As in glauconite surface coatings and attributed that to the mineral´s high sorption capacity. This is supported by Spoljaric and Crawford (1978) who found a nearly quantitative As retention from basic solution when filtering it through greensand containing 80 % glauconite. Hence, the mineral has the potential to act as As sink and source, as was suspected in an earlier study (Banning 2008). Nevertheless, to the authors´ knowledge and despite all these indications, no distinct mechanism for As uptake by glauconite is known so far. Independent from its role in As behaviour, it has been shown that glauconite loses large amounts of Fe to solution during weathering (Courbe et al. 1981, Patyk-Kara et al. 2008, Hutton and Seelye 1941). Thus, it is probable that glauconite from the primary reduced facies of the Grafenberg-layers is the major source for Fe accumulations in the oxidized near-surface part.

498 Siderite mostly represents secondary precipitates in reducing environments (Fisher et al. 1998). In
499 marine milieu, it may be formed during early diagenesis and then contributes to the sediment cement,
500 partly replacing calcite, and can be accumulated to concretionary levels (Hounslow 2001). Siderite has
501 the potential to strongly sorb As(V) at circumneutral pH conditions (Jönsson and Sherman 2008).
502 However, the affinity towards As(III) is much weaker and it can be assumed that As in the primary
503 facies of the Grafenberg-layers was mainly present as As(III) during deposition and diagenesis as well
504 as under present hydrochemical conditions (pH around 7.6, Eh around -50 mV; Mäurer and Wisotzky
505 2007). Consequently, formation of siderite in such a milieu does not retain significant As quantities
506 (Tufano and Fendorf 2008) although it cannot be excluded that the carbonate may act as a secondary
507 sink in adequate redox niches. Supporting the former, analysis of siderite concretions from a
508 geological environment very similar to the Grafenberg-layers yielded low As contents (Banning et al.
509 2009).

510 Natural pyrite is well-known for its ability to host As and numerous other minor and trace elements.
511 An overview is given by Abraitis et al. (2004). Arsenic in pyrite is commonly present at µg g^{-1} to wt.%
512 levels with a measured peak value of almost 10 wt.%. In contrast to the Fe minerals introduced before,
513 arsenic is incorporated into the pyrite structure by substitution of S. In particular, pyrites formed under
514 relatively low temperatures can have strongly elevated As. They often show habits arguing for rapid
515 precipitation, e.g. framboids, which have a reactive surface area 4-6 times larger than euhedral (cubic)
516 pyrite grains (Merinero et al. 2009), explaining high As and other element enrichments. Huerta-Diaz
517 and Morse (1990) introduced the term "degree of trace metal pyritization" (DTMP) to assess the
518 importance of incorporation of different trace metals into sedimentary pyrite. They found that the
519 disulphide is an important sink for As, Hg and Mo which are rapidly and essentially completely taken
520 up by pyrite. The sink function is significant, but less important, for Co, Cu, Mn and Ni and "generally
521 unimportant" for Cr, Pb, Zn and Cd, although at least for Pb and Zn, contents close to 1 wt.% have
522 been detected in pyrite (Abraitis et al. 2004).

523 Considering this discussion on the identified reduced Fe phases and their potential impact on As
524 behaviour, framboidal pyrite is suspected to represent the main As host in the reduced deep part of the
525 Grafenberg-layers and thus, the source of As accumulation in the oxidized upper facies. To check this

526 hypothesis, relationships between Fe, S and As were analyzed for these sediments (Fig. 8). In the Fe-S
527 scatter plot (Fig. 8a), the line of stoichiometric pyrite was implemented for comparison. Most samples
528 plot along a line parallel to that. The shift from the pyrite line indicates "excess Fe" hosted by further
529 Fe phases. This is attributable to glauconite and, to a lesser extent, siderite, being present in relatively
530 homogenous concentrations in the reduced samples. Two distinct outliers were identified, samples
531 GW_0201 and GW_0212. To reiterate, GW_0201 is the only sample to contain goethite (interpreted to
532 derive from the redox transition zone), GW_0212 is the sample showing by far the highest glauconite
533 content (11.1 %, compared to an average of 2 % in the other samples analyzed by XRD). These results
534 were accounted for in the As-S scatter plot (Fig. 8b). Samples yielding a pyrite-like development in
535 figure 8a showed a very close As-S correlation of R^2=0.94, whereas the total dataset, including the
536 outliers, only provided R^2=0.56. This indicates that pyrite is indeed the major As host in large parts of
537 the reduced Grafenberg-layers. Nevertheless, it also suggests that glauconite, if available in larger
538 quantities, is able to adsorb at least part of the As to its surface. Furthermore, it is probable that
539 goethite, derived from oxidation of Fe(II) phases, is an important As sink in the redox transition zone.
540 Here, also siderite may act as a secondary host mineral as it is present in significant quantities and As
541 is likely to at least partly occur as As(V).

542 Assuming that all As is bound in pyrite and using whole rock As and sediment pyrite contents as
543 determined by Rietveld analysis, it is possible to calculate maximum As contents in pyrite. Ignoring
544 the outliers, an average value of 0.21 ± 0.04 wt.% As_{pyr} has resulted which plots in the range of As_{pyr}
545 given by Abraitis et al. (2004) and is very similar to the average As_{pyr} value (0.23 wt.%) in a limestone
546 aquifer studied by Price and Pichler (2006).

547

548 Figure 8: Fe-S scatter plot for the reduced part of the Grafenberg-layers (a), As-S scatter plot of the same
549 samples (b).

550

551 All these considerations indicate a secondary As enrichment in the near-surface Grafenberg-layers, i.e.
552 an accumulation long after original deposition of the sediments in Oligocene times. The paleo-redox
553 process under terrestrial conditions in late Miocene/Pliocene (chapter 1.2.2) caused mobilization of Fe

554 (mainly from glauconite) and As (mainly from pyrite) and reaccumulation in the upper part. The fact
555 that in large part, Fe and As are probably from different sources may have contributed to the lack of
556 Fe-As correlation in the oxidized sediments. Trace metals showing stronger relationships with Fe, i.e.
557 Cd, Zn and Cr, belong to the group of heavy metals not preferentially accumulated in pyrite (Huerta-
558 Diaz and Morse 1992). Instead, at least Zn and Cr are known to be potentially enriched in glauconite
559 (Dooley 1998) and like Fe, may have derived in largest part from the weathering of this mineral.

560 Consequently, heterogenous distribution of Fe, As and trace metals results from mobilization through
561 oxidation, transport and subsequent reaccumulation up to concretionary levels; existing and missing
562 interrelationships of elements can be attributed to different primary sources.

563

564 4.2 Scale of accumulation

565 In order to assess the degree of As accumulation in the Fe (hydr)oxidic sediments of both study areas
566 and to estimate its relative importance compared to other trace elements, two approaches were applied
567 as used for heavy metals in dam reservoir bottom sediments by Loska et al. (1997) and for As in soils
568 by Loska et al. (2003): Enrichment Factor (EF) and cumulative Contamination Factor (CF).

569 The EF is used to evaluate element contents in the studied environment in relation to a reference
570 environment (Eq. 1).

571 $$EF = \frac{C_{sam}}{C_{ref}} \Big/ \frac{B_{sam}}{B_{ref}} \qquad \text{(Equation 1)}$$

572 where

573 C_{sam} is the concentration of the examined element in the studied environment

574 C_{ref} is the concentration of the examined element in the reference environment

575 B_{sam} is the concentration of the reference element in the studied environment

576 B_{ref} is the concentration of the reference element in the reference environment

577 EF < 2 characterize element depletion to minimal enrichment, EF=2-5 moderate enrichment and
578 EF=5-20 significant enrichment (Loska et al. 2003). The reference element used for normalization

579 must be of low variability and present in trace amounts. Alternatively, elements occurring in higher
580 concentrations can be used if they do not show any correlation towards the examined elements.
581 Fulfilling the latter condition in this study, Mg was used as a reference element for the Jurassic Fe ores
582 and Al for the oxidized Tertiary sediments (Fig. 7). Reference environments were defined as the
583 average of non-ore sediments in the Jurassic profile, weighed according to their thicknesses, and the
584 reduced part of the Grafenberg-layers, respectively.

585 The CF is applied to evaluate the impact of single contaminants on an environment. It is used to
586 identify major pollutants and to estimate the total degree of contamination, mainly of anthropogenic
587 nature, compared to pre-industrial times (Loska et al. 1997; Eq. 2).

588 $$CF = \frac{C_{av}}{C_0} \qquad \text{(Equation 2)}$$

589 where

590 C_{av} is the average content of the examined element in the studied environment

591 C_0 is the pre-industrial content of the examined element

592 Like for EF, "pre-industrial" contents in this study are equal to "pre-enrichment" contents, i.e. non-ore
593 sediment layers in the Jurassic profile and the original reduced facies of the Tertiary sediments were
594 defined as reference environments. Summing up the CFs of all contaminants allows for estimating the
595 contribution of single elements to the total contamination of the examined environment. This method
596 offers a potential impact appraisal as only bulk concentrations and no information on element mobility
597 or actual availability are included.

598

599 4.2.1 Jurassic Fe ores

600 Results for EF and CF calculations for the Jurassic Fe ores are shown in Figure 9. Enrichment factors
601 are presented for all Fe ore samples and the six most enriched trace elements, contaminations factors
602 were calculated for average contents of all Fe ore samples and the relative contribution of each heavy
603 metal to the overall "contamination pool" was deduced.

Figure 9: Enrichment Factors of 6 elements for Jurassic Fe ore samples. Pie chart: Single elements´ contribution to total "contamination pool" (UOL: upper ore layer, LOL: lower ore layer; HEL: Haupterzlager, main Fe ore body).

Copper and Pb show average EF of 0.76 and 1.39, respectively. Therefore, they are not enriched in the Fe ores. Cadmium is not included in the calculations because contents in the reference environment are broadly below or close to the analysis detection limit (0.3 µg g^{-1}). Nevertheless, ore samples have an average Cd content of 1.5 µg g^{-1}, suggesting the element´s (in this case not quantifiable) enrichment. EF average values for Zn (2.11), Ni (2.21), Co (2.30) and Cr (2.41) indicate very moderate accumulation in ore layers. While Co and Ni are evenly distributed, Cr and Zn are preferably enriched in HEL. Manganese is accumulated to a higher level (average EF=3.91), where highest values are reached in the UOL. However, arsenic is the most enriched element, yielding an average EF of 6.36 and being the only trace element plotting in the "significant enrichment" category of EF. While the factors are relatively stable within the thinner ore layers (UOL=7.48, LOL=4.97), they are variable in HEL (EF=2.6-12.7), indicating shifting degrees of favourability for As accumulation during main ore body deposition. Consequently, the studied ooidic Fe-rich sediments do not only contain significant amounts of As – they also seem to favour As uptake over heavy metals. Ruling out Mn, which has been shown to reside in the calcite matrix (chapter 4.1.1), and thus only regarding elements hosted in Fe ooids, arsenic enrichment potential is ~3 times higher than that of heavy metals. This finding is supported by CF calculations showing that As accounts for 29 % of the "contamination pool" and thus is the by far most important "pollutant" (Fig. 9, pie chart).

4.2.2 Tertiary sediments

Results of EF, ordered by Fe enrichment factor (values not shown) and CF calculations are shown in Figure 10.

Figure 10 Enrichment Factors of 6 elements for samples from the oxidized part of the Grafenberg-layers. Upper pie chart: single elements´ contribution to total "contamination pool" in one Fe hydroxide concretion, lower pie chart: single elements´ contribution to total "contamination pool" of oxidized sand samples without concretions. Note changes of scale on the x-axis.

The pronounced heterogeneity in the oxidized sediments is underlined once more when regarding EF values, even if concretion GG_0103 is ruled out. Lead, Cr and Cu, nevertheless, are constantly quite low (average values around 1, none is exceeding 2) and thus show no enrichment compared to the reduced deeper sediments. Like for the Jurassic rocks, Cd was not included in the calculations due to numerous samples in both redox facies showing contents below the detection limit. The other metals are more variable in accumulation behaviour ranging from depletion to moderate enrichment: Ni (0.4-6.6), Co (0.5-7.0), Mn (0.4-3.9), As (0.5-3.9), Zn (0.5-8.6). However, a general trend towards higher overall heavy metal enrichment coming with increasing Fe EF is observable, although not comprehensible for single elements. This situation results in relatively balanced contributions of single metals to the total "contamination pool" (Fig. 10, lower pie chart), where As has a proportion of 12 %. Calculating these proportions for the most Fe-rich concretion, the findings are completely different: here, arsenic is by far the most important contributor, accounting for 58 % of the total contaminant pool (Fig. 10, upper pie chart). An EF of 166 for As confirms extremely high accumulation. Although to a lesser extent, other metals are at least significantly enriched with EFs in the range of 10-50. It is most probable that highly enriched concretions like that are very abundant in the oxidized facies of the Grafenberg-layers, also in larger sizes than the exemplar analysed in this study (Fig. 4). Quaas (1917) describes occurrences of banked "dark iron sandstone containing hard Fe concretions" from several former quarries backfilled today and thus unfortunately not accessible for sampling anymore.

From these findings, it can be concluded that during elemental redistribution after the paleo-redox event, arsenic was initially not preferentially adsorbed to the ubiquitary Fe hydroxides coating the quartz grains in the oxidized zone. These coatings only offer a limited number of sorption sites which were not renewed as further hydroxide attachment did not happen. The sites available were probably occupied by more abundant, competing phosphate ions as suggested by a close correlation between Fe and P in the bulk sediments (Fig. 7b). Moreover, it is known that rapidly formed Fe oxyhydroxides at pH>6.5 can precipitate without significant As adsorption to the fresh surfaces (Peters 2000).

662 Relatively high pH should have prevailed during weathering due to calcite dissolution from the
663 original facies, leading to fast and ubiquitary precipitation of Fe coatings without elevated As around
664 quartz grains. Nevertheless, when it came to formation of Fe concretions in the course of ongoing
665 oxidation, arsenic was favoured for adsorption over other elements. Continuous replenishment of Fe
666 made sure that fresh Fe hydroxide precipitates constantly offered new reactive surfaces for arsenate
667 complexation, while oxyhydroxides slowly aged, i.e. polymerization led to higher degrees of
668 crystallinity. This is supported by As being dominantly present in hardly extractable fractions in
669 concretions, whereas higher proportions of NH_4-oxalate soluble As were detected for the non-
670 concretion sediments (Fig. 6b). In this late stage of the weathering process, buffer function of calcite
671 probably became unimportant because of calcite supply running short. This led to decreasing pH
672 values, allowing for slower Fe precipitation and thereby higher As accumulation (Peters 2000). It can
673 be assumed that calcite depletion was a quite rapid process, because even in the redox transition zone
674 tapped by the borehole, calcite was depleted by 95 %, compared to the reduced deeper sediments,
675 while glauconite and pyrite contents remained on the same level. Calcite dissolution in this zone may
676 also provide CO_3^{2-} for the observed intensified siderite formation (Fig. 3). In consequence, large
677 amounts of Fe and As would still have been available for precipitation after the period of pH
678 buffering. This genetic model would explain the heterogenous As distribution in the sediments and
679 allocate the formation of rather punctiform high As enrichments to a late stage of the weathering
680 process.

681

682 4.3 Implications for potential As remobilization

683 4.3.1 Jurassic sediments

684 Presently, groundwater milieu around the former quarry Kahlenberg is oxidizing. An artificial lake,
685 located 1 km downstream of the quarry in highly conductive Quaternary gravels ($K = 1*10^{-2} – 1*10^{-3}$
686 m/s) is in proven hydraulic contact with the Jurassic Fe ores. Nevertheless, transport of As or other
687 contaminants was not detected so far (LGRB 2001), and Fe concentrations are constantly below 0.02
688 mg L^{-1} in wells (information from local water supplier), indicating no output from the ores. This is in

689 good agreement with general hydrochemical conditions in Middle Jurassic aquifers of the region (Tab.
690 6). Average readily ($NH_4H_2PO_4$-) soluble As was calculated for UOL, LOL and HEL, applying
691 thickness-weighted mean values, to be 4.8 µg g^{-1}. Assuming a change to reducing redox conditions,
692 the average short- to medium-term mobilizable As amount (steps 1-3) would be 15.9 µg g^{-1}. With an
693 average density of 3.3 g cm^{-3} (calculated for an average mineral composition), this would equal ~16 g
694 m^{-3} of easily soluble As and ~52 g m^{-3} of potentially soluble As in the ores. Although it was shown
695 that As is mainly hosted by Fe ooids (chapter 4.1.1), it cannot be excluded that a minor part of reactive
696 As is present in the matrix, since SEP analysis was conducted for whole rock samples. Nevertheless,
697 this proportion seems to be negligible as no As was found in downstream groundwater. To access the
698 pool of potentially mobile As, i.e. to make contact with As-rich Fe ooids, water would have to solve
699 the calcite matrix first and then would only be successful in leaching As when bringing reducing
700 conditions along. Both is hardly possible under present physico- and hydrochemical conditions in the
701 aquifer, which is supported by very low Fe and As background values in groundwater (Tab. 6). The
702 risk of As remobilization is estimated to be generally insignificant under present conditions because of
703 an oxidizing and circumneutral groundwater milieu, arsenic being trapped in hardly extractable
704 mineral fractions and the "protection function" of the As-poor calcite matrix.

705

706 Table 6: Typical groundwater chemistry in the studied aquifers.
707

708 4.3.2 Tertiary sediments

709 Step 1-soluble As in the reduced part of the Grafenberg-layers is 0.8 µg g^{-1} on average, leading to an
710 amount of ~1.8 g m^{-3} sediment. It was shown in chapter 4.1.2 that As in these sediments is largely
711 hosted by pyrite. Thus, it must be assumed, at least for a worst case szenario, that sediment bulk As is
712 potentially mobilizable when oxidizing conditions arise. In such an aquifer milieu, pyrite can dissolve
713 rapidly and thereby release its As to solution (Jones and Pichler 2007). This process may even be
714 accelerated, relative to pure pyrite, when significant As contents are present in the lattice (Savage et al.
715 2000). Thus, an As content of 11.6 µg g^{-1} is potentially mobilizable, corresponding to ~27 g m^{-3}
716 sediment. Mäurer and Wisotzky (2007) found that present groundwater milieu in the vicinity of the

717 sampled borehole is reducing below a depth of ~35-40 m below ground surface, thus correlating well
718 with the proposed redox transition zone derived from geochemical results of this study. Below that
719 depth, water is undersaturated with respect to $Fe(OH)_3$ and around SI=0 for $FeCO_3$, both change to
720 significant oversaturation around 40 m. This data modelled by Mäurer and Wisotzky (2007) is in good
721 agreement with the mineralogical findings in this work. Consequently, pyrite is rather stable and thus
722 should not be an active As source under the given conditions. Nevertheless, in spite of their rather low
723 hydraulic conductivity of $4.2*10^{-5}$ m/s on average (Mäurer and Wisotzky 2007), the Oligocene
724 sediments are used for drinking water extraction. In a pumping well near the sampled outcrops, the
725 groundwater table is lowered by up to 25 m during pumping. It was described in chapter 1.2.2 that the
726 depth of the paleo-redox boundary is variable in the study area, but mostly around 20-30 m below
727 ground surface. Therefore, groundwater extraction might change redox conditions to rather oxidizing
728 in the top of the reduced primary facies, thus enabling Fe(II) phases dissolution and output of Fe and
729 hosted As into solution. It is unlikely that this happened in case of the mentioned pumping well, with
730 the raw water showing stable Fe concentrations and As constantly below the detection limit
731 (information from local water supplier). Nevertheless, the redox boundary should be considered when
732 constructing and operating pumping wells in the area. A clear positive correlation between Fe and SO_4
733 as well as an increase of both parameters in deep wells of one waterworks in the study area since the
734 start of water extraction from the Grafenberg-layers as described by Mäurer and Wisotzky (2007) hints
735 towards successive pyrite oxidation and thus, potential As mobilization. Although no critical As
736 concentrations have been measured so far, continuous groundwater monitoring for As and other
737 potential contaminants is mandatory. An additional problem arises from the surface input of
738 agricultural nitrate being transported to deeper aquifers and triggering pyrite oxidation therein. This
739 phenomenon was described by Cremer et al. (2003) for a fluvial Pliocene aquifer in the vicinity of the
740 study area. They measured groundwater As concentrations up to 130 µg L^{-1} and identified pyrite as the
741 As source. It has also been shown from other regions that anthropogenic disturbance of subsurface
742 redox conditions in an aquifer containing pyrite as a trace mineral and yielding average bulk sediment
743 As even below the values in this work, can lead to significantly elevated As concentrations in
744 groundwater (Price and Pichler 2006).

Due to the very heterogenous element distribution and limited number of samples in the upper part, calculations for potential As mobilization must be considered a rough estimate. In the oxidized facies, unconsolidated sands show an average of 0.9 µg g^{-1} step 1-soluble As, corresponding to ~2.2 g As per m^3 sediment. For Fe hydroxide concretions, the $NH_4H_2PO_4$-soluble As is 8.9 µg g^{-1} on average, resulting in ~28 g m^{-3}. Assuming a concretion proportion of 1 % of the total sediment, concluded from own observations in outcrops and earlier geological descriptions (Quaas 1917), an average value for bulk oxidized sediment may be calculated: 2.5 g m^{-3}. Thus, ~12 % of the total easily mobilizable As in bulk sediments is contributed by concretions. Conducting these calculations for potentially short- to medium-term soluble As, sands yield 5.5 µg g^{-1} (~12 g m^{-3}) and concretions 20.8 µg g^{-1} (~67 g m^{-3}) on average. Bulk sediment would have 12.6 g m^{-3}. Here, concretions contribute only ~5 % to the potentially mobilizable As pool. This can be attributed to the higher degree of hydroxide crystallinity as indicated in chapter 4.2.2. Calculated As values for concretions are very similar to those established for the Jurassic Fe ores (chapter 4.3.1). But in contrast to those, the As bound to concretions is much better available for water-rock-interaction as the sands hosting the Fe accumulations represent an unconsolidated pore aquifer allowing for larger contact areas. Surface-bound As in the bulk oxidized part (2.5 g m^{-3}) is slightly higher than in the reduced facies (1.8 g m^{-3}). The larger pool of short- to medium-term mobilizable As in the near-surface sediments, however, will only be accessible for solution if reducing groundwater conditions occur. Therefore, depth-dependent Eh monitoring in wells is recommendable for water suppliers.

Comparing both redox facies of the Grafenberg-layers in terms of risk assessment for As remobilization from sediments, the reduced deeper material has a higher potential for causing elevated As concentrations in groundwater. It is more probable for pyrite-oxidizing conditions to reach the primary facies as a consequence of groundwater extraction or nitrate input then for the As hosted in the oxidized facies to be dissolved under reducing conditions (the latter may be imaginable in the course of rising groundwater table or input of organic matter into the system triggering microbiologically induced reduction). Moreover, the reduced part hosting As-laden pyrite in a relatively homogenous distribution would act as an As area source, thus potentially releasing bulk sediment As to solution. In contrast, the source function in the oxidized facies is rather punctual.

773 Showing partly very high As accumulations, the hosting Fe hydroxide concretions occur rather locally.
774 Nevertheless, they contribute a measurable proportion to bulk sediment reactive As, yet the absolute
775 addition is not significant enough to substantially rise this pool. Additional information on the
776 distribution, amount and geochemistry of these Fe concretions would be needed to better quantify their
777 impact on As behaviour in the study area.

778 The groundwater background As concentration in the study area is 1.5 µg L^{-1} (LUA NRW and
779 MUNLV 2000; Tab. 6). If we assume that this is caused by solution of surface-bound As from
780 Tertiary rocks (~2 g m^{-3}), we can calculate that, referring to 1 m^3 sediment (with a known effective
781 drainage porosity of n_f=0.13; Mäurer and Wisotzky 2007), approximately 10000 pore volumes are
782 needed to produce the background concentration. Further assuming bulk As solubility (~27 g m^{-3}) in
783 the reducing sediments, i.e. generation of an oxidizing milieu, this water volume would produce an As
784 groundwater concentration of ~21 µg L^{-1}, thus exceeding threshold guidelines by more than factor 2.
785 Again, this calculation must be regarded a rough estimation which, nevertheless, points to the
786 significant impact of changing redox conditions on As concentration in groundwater.

787

788 5 Conclusions

789 Two different As accumulation processes have been identified in Jurassic Fe ores (Aalenian/Bajocian)
790 at the margin of the Upper Rhine Graben and in Tertiary sediments (Grafenberg-layers, Chattian) in
791 the Lower Rhine Embayment. The primal As input into the study areas, both of which are
792 characterized by shallow marine deposition, was accomplished by terrestrial weathering of Variscan
793 mainlands (first-order sources). Primary, i.e. syndepositional, enrichment is responsible for the
794 Jurassic Fe ores showing high As which is hosted by mainly goethite ooids (first-order sinks/second-
795 order sources). While these ooids were slowly formed during condensed sedimentation under mainly
796 oxidic conditions, thereby offering reactive surfaces for accumulation, arsenic in the Oligocene
797 sediments was enriched in a reducing milieu and is mainly hosted by framboidal pyrite (first-order
798 sinks/second-order sources). Secondary As accumulation, i.e. during element redistribution in a late
799 stage of a paleo-redox event in the late Tertiary, led to partly high As in Fe hydroxide concretions

(second-order sinks/third-order sources) occurring in near-surface Tertiary sands. Both accumulation processes favoured As enrichment over other contaminants, underlining preferential As sorption on Fe hydroxides. In spite of higher bulk As in oxidic rocks, i.e. Jurassic ooidic ores and Fe oxihydroxide concretions in the upper Tertiary redox facies, the mainly pyrite-hosted As pool within the reduced deeper part of the Grafenberg-layers has been shown to be the most probable candidate for potentially creating elevated As concentrations in groundwater, especially if the present redox milieu is anthropogenically disturbed through groundwater extraction.

This study highlights the importance of geological processes millions of years ago for present day distribution (sources and sinks) and availability of potential groundwater contaminants, especially As. Moreover, it underlines the necessity to assess risks arising from single contaminants not on the basis of bulk contents alone, but also to account for the element fractionation as well as the present hydrogeochemical situation. The comprehension and distinction of geological As accumulation processes provides the basis for understanding and forecasting As behaviour in natural systems.

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7 References

Abraitis, P.K., Pattrick, R.A.D. and Vaughan, D.J. (2004) Variations in the compositional, textural and electrical properties of natural pyrite: a review. International Journal of Mineral Processing 74, 41-59.

826 Acharyya, S.K., Lahiri, S., Raymahashay, B.C. and Bhowmik, A. (2000) Arsenic toxicity of
827 groundwater in parts of the Bengal basin in India and Bangladesh: the role of Quarternary
828 stratigraphy and Holocene sea-level fluctuation. Environmental Geology 39, 1127-1137.

829 Aldinger, H. (1957) Eisenoolithbildung und rhythmische Schichtung im süddeutschen Jura [Iron oolith
830 formation and rhythmic stratification in the Jurassic of southern Germany]. Geologisches
831 Jahrbuch 74, 87-96.

832 Armienta M.A., Villaseñor G., Rodriguez R., Ongley L.K. and Mango H. (2001) The role of arsenic-
833 bearing rocks in groundwater pollution at Zimapán Valley, México. Environmental Geology
834 40, 571-581.

835 Banning, A. (2008) Bog Iron Ores and their Potential Role in Arsenic Dynamics: An Overview and a
836 "Paleo Example". Engineering in Life Sciences 6, 641-649.

837 Banning, A., Coldewey, W.G. and Göbel, P. (2009) A procedure to identify natural arsenic sources,
838 applied in an affected area in North Rhine-Westphalia, Germany. Environmental Geology 57,
839 775-787.

840 Barringer, J.L., Bonin, J.L., Reilly, P.A., Szabo, Z. and McGee, C.K. (2009) Sources of Arsenic to
841 Streams of the inner Coastal Plain of New Jersey, USA. GSA Northeastern Section – 44th
842 Annual Meeting, 22-24 Mar 2009, Portland, Maine.

843 Bayer, M. (1997) Natürliche Arsenanreicherungen in der Oberen Süßwassermolasse Bayerns [Natural
844 arsenic accumulations in the Upper Süßwassermolasse of Bavaria]. Veröffentlichungen des
845 Grundbauinstitutes der Landesgewerbeanstalt Bayern 77, 250 pp.

846 Bayer, U. (1970) Das Profil des Erz-Tagebaus Ringsheim (Ober-Aalenium/Unter-Bajocium) [The
847 geological profile of the Ringsheim ore quarry (Upper Aalenian/Lower Bajocian)]. Neues
848 Jahrbuch für Geologie und Paläontologie, Monatshefte 1970, 261–269.

849 Berner, R.A. (1981) New geochemical classification of sedimentary environments. Journal of
850 Sedimentary Petrology 51, 359-365.

851 Burkhalter, R.M. (1995) Ooidal ironstones and ferruginous microbialites: origin and relation to
852 sequence stratigraphy (Aalenian and Bajocian, Swiss Jura mountains). Sedimentology 42, 57-
853 74.

854 Cappuyns, V., Swennen, R. and De Nil, K. (2002) Heavy metals and arsenic in alluvial sediments of
855 the Grote Beek river (N Belgium): Contribution of natural and anthropogenic sources.
856 Aardkundige Mededelingen 12 (Proceedings of the first Geologica Belgica International
857 Meeting, 11-15 Sep, Leuven, Belgium 2002), 227-230.

858 Courbe, C., Velde, B., and Meunier, A. (1981) Weathering of glauconites: Reversal of the
859 glauconitization process in a soil profile in western France. Clay Minerals 16, 231-243.

860 Cremer, N., Obermann, P. and Wisotzky, F. (2003) Mobilization of Nickel, Cobalt and Arsenic in a
861 Multi-aquifer Formation of the Lower Rhine Valley: Identification and Modeling of the
862 Processes Controlling Metal Mobility. In: Schulz, H.D. and Hadeler, A. (Eds.) Geochemical
863 Processes in Soil and Groundwater – Measurement – Modelling – Upscaling (Proceedings
864 GeoProc2002), 3-18, Wiley, Weinheim.

865 Dooley, J.H. (1998) Comprehensive Chemistry of Select Greensand from the New Jersey Coastal
866 Plain. The New Jersey Geological Survey Technical Memorandum 98-1, 20 pp.

867 Fisher, Q.J., Raiswell, R. and Marshall, J.D. (1998) Siderite concretions from nonmarine shales
868 (Westphalian A) of the Pennines, England: Controls on their growth and composition. Journal
869 of Sedimentary Research 68(5), 1034-1045.

870 Flügel, E. (2004) Microfacies of Carbonate Rocks. Analysis, Interpretation and Application. 976 pp.,
871 Springer, Berlin.

872 GLA NRW (Geologisches Landesamt Nordrhein-Westfalen, Ed., 1988) Geologie am Niederrhein
873 [Geology of the Lower Rhine area], 142 pp., Krefeld.

874 Halbach, P. (1968) Zum Gehalt von Phosphor und anderen Spurenelementen in Brauneisenerzooiden
875 aus dem fränkischen Dogger beta [On the phosphorous and other trace elements contents in

876 goethite ore ooids from the Franconian Dogger beta]. Contributions to Mineralogy and
877 Petrology 18, 241-251.

878 Heinrichs G. and Udluft P. (1996) Geogenes Arsen in Grundwässern Deutschlands unter
879 Berücksichtigung der Aquifergeologie [Geogenic arsenic in German groundwater with respect
880 to aquifer geology]. Zeitschrift der Deutschen Geologischen Gesellschaft 147, 519-530.

881 Heinrichs G. and Udluft P. (1999) Natural arsenic in Triassic rocks: a source for drinking water
882 contamination in Bavaria, Germany. Hydrogeology Journal 7, 468-476.

883 Hiss, M., Jansen, F. and Prüfert, J. (2005) Das Tertiär des Niederrheins in der Stratigraphischen
884 Tabelle von Deutschland 2002 [The Tertiary of the Lower Rhine area in the stratigraphic chart
885 of Germany 2002]. Newsletters on Stratigraphy 41(1-3), 307-312.

886 Hounslow, M.W. (2001) The crystallographic fabric and texture of siderite in concretions:
887 implications for siderite nucleation and growth processes. Sedimentology 48(3), 533-557.

888 Huerta-Diaz, M.A. and Morse, J.W. (1990) A quantitative method for determination of trace metal
889 concentrations in sedimentary pyrite. Marine Chemistry 29, 119-144.

890 Huerta-Diaz, M.A. and Morse, J.W. (1992) Pyritization of trace metals in anoxic marine sediments.
891 Geochimica et Cosmochimica Acta 56, 2681-2702.

892 Hutton, C.O. and Seelye, F.T. (1941) Composition and properties of some New Zealand glauconites.
893 American Mineralogist 26(10), 595-604.

894 Jones, G.W. and Pichler, T. (2007) Relationship between Pyrite Stability and Arsenic Mobility during
895 Aquifer Storage and Recovery in Southwest Central Florida. Environmental Science &
896 Technology 41(3), 723-730.

897 Jönsson, J. and Sherman, D.M. (2008) Sorption of As(III) and As(V) to siderite, green rust (fougerite)
898 and magnetite: implications for arsenic release in anoxic groundwaters. Chemical Geology
899 255(1-2), 173-181.

LGRB (Landesamt für Geologie, Rohstoffe und Bergbau Baden-Württemberg) (Ed., 2001) Wechselwirkungen zwischen Baggerseen und Grundwasser [Interactions between artificial lakes and groundwater]. LGRB Informationen 10, 64 pp., Freiburg.

LGRB (Landesamt für Geologie, Rohstoffe und Bergbau Baden-Württemberg) (Ed., 2009) Natürliche Geogene Grundwasserbeschaffenheit in den hydrogeochemischen Einheiten von Baden-Württemberg [Natural geogenic groundwater quality in the hydrogeochemical units of Baden-Württemberg]. LGRB Informationen 23, 192 pp., Freiburg.

Loska, K., Cebula, J., Pelczar, J., Wiechuła, D. and Kwapulinski, J. (1997) Use of enrichment, and contamination factors together with geoaccumulation indexes to evaluate the content of Cd, Cu, and Ni in the Rybnik water reservoir in Poland. Water, Air, and Soil Pollution 93, 347-365.

Loska. K., Wiechuła, D., Barska, B., Chebula, E. and Chojnecka, A. (2003) Assessment of Arsenic Enrichment of Cultivated Soils in Southern Poland. Polish Journal of Environmental Studies 12, 187-192.

Lowers, H.A., Breit, G.N., Foster, A.L., Whitney, J., Yount, J., Uddin, M.N. and Muneem, A.A. (2007): Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh. Geochimica et Cosmochimica Acta 71, 2699-2717.

LUA NRW and MUNLV (Landesumweltamt Nordrhein-Westfalen and Ministerium für Umwelt und Naturschutz, Landwirtschaft und Verbraucherschutz des Landes Nordrhein-Westfalen (Eds., 2000)) Grundwasserbericht NRW 2000 [Groundwater report for North Rhine-Westphalia].

Matschullat, J. (1999) Arsen in der Geosphäre [Arsenic in the geosphere]. In: Rosenberg, F. and Röhling, H.G. (Eds.) Arsen in der Geosphäre. Schriftenreihe der Deutschen Geologischen Gesellschaft 6, 5-20.

Mäurer, D. and Wisotzky, F. (2007) Zukünftige Entwicklung des Tiefengrundwassers am Standort eines Wasserwerkes am Niederrhein [Future development of deep groundwater at the location of a waterworks in the Lower Rhine area]. Bochumer Geowissenschaftliche Arbeiten 11, 60-70.

927 Maynard, J.B. (1983) Geochemistry of Sedimentary Ore Deposits. 305 pp., Springer, Berlin.

928 Merinero, R., Lunar, R., Somoza, L., Díaz-Del-Río, V. and Martínez-Frías, J. (2009) Nucleation,
929 growth and oxidation of framboidal pyrite associated with hydrocarbon-derived submarine
930 chimneys: lessons learned from the Gulf of Cadiz. European Journal of Mineralogy 21, 947-
931 961.

932 Nickel, E. (2003) Oligozäne Beckendynamik und Sequenzstratigraphie am Südrand des
933 Nordwesteuropäischen Tertiärbeckens [Oligocene basin dynamics and sequence stratigraphy
934 on the southern margin of the Northwest European Tertiary Basin]. Ph.D. thesis, 151 pp.,
935 Bonn.

936 Patyk-Kara, N.G., Dubinchuk, V.T., Levchenko, M.L. and Andrianova, E.A. (2008) Composition of
937 Glauconite from the Upper Cretaceous Sedimentary Formation in Central Regions of Russia.
938 Doklady Earth Sciences 423A(9), 1388-1390.

939 Peters, S.C. (2000) Arsenic Concentrations and Iron Oxyhydroxide Formation in New Hampshire
940 Groundwater. AGU 2000 Fall Meeting, 15-19 Dec 2000, San Francisco, USA.

941 Price, R.E. and Pichler, T. (2006) Abundance and mineralogical association of arsenic in the
942 Suwannee Limestone (Florida): Implications for arsenic release during water-rock interaction.
943 Chemical Geology 226, 44-56.

944 Quaas, A. (1917) Erläuterungen zur Geologischen Karte von Preußen und benachbarten
945 Bundesstaaten, Blatt 4704 Viersen [Explanations on the geological map of Prussia and
946 neighbouring states, map sheet 4704 Viersen]. 70 pp., Berlin.

947 Ravenscroft P., Burgess W.G., Ahmed K., Burren M. and Perrin J. (2005) Arsenic in groundwater of
948 the Bengal Basin, Bangladesh: Distribution, field relations, and hydrogeological setting.
949 Hydrogeology Journal 13, 727-751.

950 Rüde, T.R. and Königskötter, H. (2009) Geogenic enrichment of arsenic in histosols. In: Bundschuh,
951 J., Bhattacharya, P., Matschullat, J. and Armienta, M.A. (Eds.) Natural arsenic in

952 groundwaters of Latin America, 285-293 (Arsenic in the Environment Vol. 1 – CRC
953 Press/Balkema, Leiden).

954 Salama, W., El Aref, M. and Gaupp, R. (2008) Origin of the autochthonous/para-autochthonous Fe
955 ooids and oncoids of the Lower Eocene ironstones, Baharia Depression, Western Desert,
956 Egypt. Geo2008 – Ressources and Risks in the Earth System, International Conference and
957 annual meeting of DGG and GV, 29 Sep-02 Oct 2008, Aachen, Germany.

958 Savage, K.S., Tingle, T.N., O'Day, P.A., Waychunas, A. and Bird, D.K. (2000) Arsenic speciation in
959 pyrite and secondary weathering phases, Mother Lode Gold District, Tuolumne County,
960 California. Applied Geochemistry 15, 1219-1244.

961 Sauer, K. and Simon, P. (1975) Die Eisenerze des Aalenium und Bajocium im Oberrheingraben
962 (Grube Kahlenberg, Grube Schönberg und kleinere Vorkommen) [Aalenian and Bajocian iron
963 ores in the Upper Rhine Graben (Kahlenberg quarry, Schönberg quarry and smaller deposits)].
964 Geologisches Jahrbuch D10, 25-68.

965 Schwertmann, U., Friedl, J. and Stanjek, H. (1999) From Fe(III) Ions to Ferrihydrite and then to
966 Hematite. Journal of Colloid and Interface Sciences 209, 215-223.

967 Siehl, A. and Thein, J. (1987) Geochemische Trends in der Minette (Jura, Luxemburg/Lothringen)
968 [Geochemical trends within the Minette iron ores (Jurassic, Luxembourg/Lorraine)].
969 Geologische Rundschau 67(3), 1052–1077.

970 Smedley, P.L. and Kinniburgh, D.G. (2002) A review of the source, behaviour and distribution of
971 arsenic in natural waters. Applied Geochemistry 17, 517-568.

972 Spoljaric, N. and Crawford, W.A. (1978) Glauconitic Greensand: A possible filter of heavy metal
973 cations from polluted water, Environmental Geology, 2(4), 215-221.

974 Stanger, G. (2005) A palaeo-hydrogeological model for arsenic contamination in southern and south-
975 east Asia. Environmental Geochemistry and Health 27, 359-367.

976 Stollenwerk, K.G. (2002) Geochemical Processes Controlling Transport of Arsenic in Groundwater: A
977 Review of Adsorption. In: Welch, A.H. and Stollenwerk, K.G. (Eds.) Arsenic in Ground
978 Water – Geochemistry and Occurrence, 67-100, Springer, New York.

979 Tessier, A., Campbell, P.G.C. and Bisson, M. (1979) Sequential Extraction Procedure for the
980 Speciation of Particulate Trace Metals. Analytical Chemistry 51(7), 844-851.

981 Tufano, K.J. and Fendorf, S. (2008) Confounding impacts of iron reduction on arsenic retention.
982 Environmental Science & Technology 42(13), 4777-4783.

983 Urban, H. (1966) Bildungsbedingungen und Faziesverhältnisse der marin-sedimentären
984 Eisenerzlagerstätte am Kahlenberg bei Ringsheim/Baden [Formation and facies conditions of
985 the marine sedimentary iron ore deposit at the Kahlenberg near Ringsheim/Baden]. Jahreshefte
986 des Geologischen Landesamtes Baden-Württemberg 8, 125-268, Freiburg.

987 Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E. and Adriano, D.C. (2001)
988 Arsenic fractionation in soils using an improved sequential extraction procedure. Analytica
989 Chimica Acta 436, 309-323.

990 Zahid, A., Hassan, M.Q., Breit, G.N., Balke, K.-D. and Flegr, M. (2009) Accumulation of iron and
991 arsenic in the Chandina alluvium of the lower delta plain, Southeastern Bangladesh.
992 Environmental Geochemistry and Health 31, 69-84.

993 Zeien H. and Brümmer G.W. (1989) Chemische Extraktionen zur Bestimmung von
994 Schwermetallbindungsformen in Böden [Chemical extractions for the determination of heavy
995 metal fractionation in soils]. Mitteilungen der Deutschen Bodenkundlichen Gesellschaft 59,
996 505-510.